INTENSITY RATIO OF PRINCIPAL-SERIES DOUBLETS OF THE ALKALI METALS

H. Jakob

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546   AUGUST 1974

1. Report No. NASA TT F-15,892	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle INTENSITY RATIO OF PRINCIPAL-SERIES DOUBLETS OF THE ALKALI METALS		5. Report Date August 1970
		6. Performing Organization Code
7. Author(s) H. Jakob, Physics Institute, University of Breslau (Wroclaw)		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASw-2481
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Über das Intensitätsverhältnis der Hauptseriendubletts der Alkalimetalle," Annalen der Physik (fourth ser.), Vol. 86, No. 12, 1928, pp. 449-493

16. Abstract   The intensity ratios between the components of the second principal-series doublets of potassium, rubidium and cesium are measured as functions of vapor density in an oxy-hydrogen flame, using a photographic/photometric method. Values between 1.80 and 2.02 are found for K. Merton's grid method of evaluating photographs is modified. Line absorption is measured by Gouy's method for the second principal-series terms of rubidium and cesium to obtain intensity-ratio limits ("true" intensity ratio). A value of 4.0 is approached by cesium. A suitable value was not obtained for rubidium, but it is concluded to be greater than 2.3.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified-Unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 48	22. Price

INTENSITY RATIO OF PRINCIPAL-SERIES DOUBLETS OF THE ALKALI METALS

Hans Jakob,
Physics Institute, University of Breslau (Wroclaw)

1. Introduction

In classical models, the total intensity (cf. [1]) of a spectral line from an infinitely thin emitting layer is proportional to the number $\mathfrak{N}$) of emitting and absorbing centers (dispersing electrons). Proportionality is assumed here between emission and absorption capacities, e.g thermal radiation. Under these conditions, the intensity ratio between two closely neighboring components of a doublet is

$$\frac{J_2}{J_1} = \frac{\mathfrak{N}_2}{\mathfrak{N}_1}. \tag{1}$$

On the other hand, according to Bohr's quantum theory, the intensity J of a spectral line of frequency ν is given by

$$J = N_m \cdot a_{m \to n} \cdot h\nu. \tag{2}$$

Here, N_m is the number of atoms in the mth state, $a_{m \to n}$ is the probability of an atom's transition from the mth to the nth state. In statistical equilibrium, e.g. for thermal excitation at temperature T,

$$N_m = G_m \cdot e^{-\frac{h\nu}{kT}} \tag{3}$$

(G_m = statistical weight of the mth state). Accordingly, the

---

* Numbers in the margin indicate pagination in the foreign text.

intensity ratio of the components of a doublet is expressed by the formula

$$\frac{J_2}{J_1} = \frac{G_{m_2}}{G_{m_1}} \cdot \frac{e^{-\frac{h\nu_2}{kT}}}{e^{-\frac{h\nu_1}{k\cdot T}}} \cdot \frac{a_{m_2 \to n}}{a_{m_1 \to n}} \cdot \frac{h\nu_2}{h\nu_1}$$

If the doublet components are close together, this equation becomes

$$\frac{J_2}{J_1} = \frac{G_{m_2}}{G_{m_1}} \cdot \frac{a_{m_2 \to n}}{a_{m_1 \to n}} \cdot \qquad (4)$$

According to the relationship given by Ladenburg [2] between transition probability and the number $\mathfrak{N}_{m \to n}$ of dispersing electrons associated with the transition m → n

$$\mathfrak{N}_{n \to m} = N_n \cdot \frac{G_m}{G_n} \, a_{m \to n} \cdot \frac{m c^3}{8\pi e^2 \nu^2} ,$$

equation (4) is identical to equation (1).

In order to determine the intensity ratio of spectral lines, we can also make use of any method of investigation which allows the ratio of the numbers of dispersing electrons to be measured.

Three methods come under consideration for measuring the number $\mathfrak{N}$, namely

a)　àlbe the measurement of anomalous dispersion in the neighborhood of the spectral line,

b)　the measurement of the magnetic rotation of the plane of polarization,

c)　absorption measurements.

A large number of measurements of intensity ratios and/or the ratio $|\mathfrak{N}_2/\mathfrak{N}_1|$ performed on the sodium vapor D-lines by all three methods were available at the beginning of this work.

Roschdestwenski [3] obtained values between 1.95 and 2.09 for the intensity ratio $D_2:D_1$ from dispersion measurements.

From measurements of the magnetic rotation of the plane of polarization performed on D-lines, H. Senftleben [4], using flames, and R. Minkowski [5], using a vapor tube, obtained a value of 2.0 for $|\mathfrak{N}_2/\mathfrak{N}_1|$ within limits of error of about 6%.

Likewise, photographic/photometric absorption measurements by Füchtbauer and Schell [6] yielded a value of 2.03. The deviation of 1.5% from 2.0 lies within the experimental precision.

As for direct measurements of J_2/J_1, i.e. emission measurements, only those by Ladenburg [2], conducted by a photographic/ /photometric method, were available for the first Na terms, aside from the spectrophotometer measurements performed by G.L. Gouy [7]. Using very weakly colored flames, the two authors obtained a value of 2.0, within the experimental range of error, decreasing with increasing flame coloration to approximately $\sqrt{2} = 1.41$.

$|\mathfrak{N}_2/\mathfrak{N}_1|$ measurements with higher principal-series terms were performed by the method of anomalous dispersion by Bevan [8] and Roschdestwenski [9] and by the absorption method by Füchtbauer et al. [10, 11]. Bevan obtained a value of 3.0 for the second Rb term (1s — 3p); Roschdestwenski's results for K, Rb and Cs are compiled in the following table:

Series b [expansion unknown]	K	Rb	Cs
$1s - 2p$	1,98	2,02	2,05
$1s - 3p$	2,05	2,58	4,07
$1s - 4p$		2,90	7,4
$1s - 5p$			9,1

[Note: Commas in numerals are equivalent to decimal points.]

In the cases of Rb and Cs, these figures show a systematic increase in the intensity ratio with term number, but not in the case of K. For K, the result is confirmed by new measurements by Prokofiyev [12], who obtained 2.04 as the mean from a large number of studies.

On the basis of the above absorption measurements performed on Cs and Rb, in which systematically increasing values of J_2/J_1 were observed with increasing term number, Füchtbauer and Bartels [11] concluded the following series law:

"For corresponding doublets of all alkali metal principal series, the intensities of the long-wavelength and short-wavelength lines are in the same ratio and this ratio is equal to 1:m for the /452 pair 1s - mp."

New experiments by Füchtbauer and Meier [13] yielded a value of ~4.0 for the third Cs term.

Due to the diverging results of the observers discussed above, I was given the task of determining the intensity ratios of higher terms of the principal-series for alkali elements by emission measurements using the photographic/photometric method; direct emission measurements for higher principal series terms were not available at the beginning of my studies[1].

The well-known, extensive studies by the Utrecht school on the intensity ratio of series lines and the principles governing them appeared during the course of my work; in particular, Burger and Dorgelo [14], generalizing the results of Dorgelo [15], Bartels [16] and others, set up a series of intensity rules. Their

---

[1] Except for a series of experiments by Gouy [7], on the basis of which he extrapolated the value 2.9 for the intensity ratio of the components of the second Rb principal-series doublet.

intensity rule III requires that for a subdivided initial and single final level, the intensity ratio of components of a multiplet is given by the ratio of the statistical weights of the initial levels, i.e. in the case of the principal series of alkali metals, has a value of 2:1 regardless of the integer variable.[2]

This rule is verified to a certain degree by the above-mentioned experiments on the first Na principal-series term. Measurements of higher terms produced contradictory results, however. Dorgelo [15] obtained a value of 1.8 for the second Cs term; Frerichs [18] obtained 2.0 for the second K term; Oudt [19] obtained 2.0 for both the second and third Rb terms; the same value for the second Cs term in the electric arc, but values between 2:1 and 5:1 in a flame of hydrogen and oxygen. My own first results [20] confirmed rule III for the second principal-series terms of K, Rb and Cs, but later, more precise experiments yielded considerably different results (cf. [21]), to be discussed in detail.[3]

On the basis of equation (4), the content of Rule III means that the ratio of transition probabilities $a_{m2 \to n}/a_{m1 \to n}$ is independent of the principal quantum number and, moreover, the transition probabilities of the individual components are independent of the inner quantum numbers that determine them. A theoretical basis has also been found for both results [23, 24].

The results discussed above from the dispersion and absorption experiments on the higher principal-series terms thus grossly

---

[2] It can be seen from measurements of splitting in the Zeeman effect within the principal series for alkali metals [17] that the weight ratio of the p-levels does not change with the principal quantum number.

[3] The studies by A. Filippov [22] which appeared during the course of my studies will also be discussed.

contradict the predictions of Rule III, but the emission measurements presented still do not permit a decision to be made. This article is intended to provide additional material for clarifying the issue.

2. Simultaneous Measurement of Intensity Ratio and Line Absorption

Measurements of the intensity ratios of principal-series terms in emission involve a basic problem which is generally known and has been emphasized: Due to absorption of the radiation of lines being studies by unexcited atoms of vapor in the light source itself, differing for the two components as a function of their different emission power, the intensity ratio is distorted and reduced with respect to its true value $(IR)_t$ for an infinitesimal number of centers. However, the principles formulated by Ladenburg and Reiche [1] and the quantum rules apply only to this $(IR)_t$. Thus the only type of light source which can be considered /454 is one which satisfies the requirements of an infinitesimal number of centers as closely as possible, by means of an extremely low vapor density and small layer thickness. Whether this condition is actually satisfied cannot be immediately stated, as was found during the course of these studies. Actual proof of this was likewise not obtained in Filippov's [22] experiments, either. Thus a special criterion had to be found for this. Such is offered by the measurement of line absorption (LA) by the method first performed by Gouy [7].

For Ladenburg and Reiche [1], LA refers to the total absorption experienced by the light of a spectral line propagating from a radiator totally equivalent to the absorbing radiator, i.e., in our case, the absorption of the flame studied for light of the lines which are emitted by a light source completely identical to the first flame. We determine LA by measuring the increase in brightness of the spectral lines studied when the luminous vapor

layer is doubled. For brightness $\bar{I}$ for a double vapor layer is given by the equation

or
$$\bar{I} = I + I(1 - A_L)$$
$$\frac{\bar{I}}{I} = k = 2 - A_L.$$

The quantity $\bar{I}/I$ is called k. Gouy [7] measured this quantity as long as 50 years ago in a ground-laying paper "Photometric studies on colored flames" for a series of alkali metals and alkaline earths as a function of line brightness I, using subjective photometry. In almost all of the cases studied, he obtained a very similar curve of k as a function of I, so a certain amount of generality can be ascribed to the results. The value of k drops from a value close to 2.0 (for "infinitely thin" flames) rather rapidly with increasing number of centers (i.e. increasing brightness) and quickly approaches a lower limit of approximately $\sqrt{2}$ (1.41); this corresponds to an LA of about 59%. The function k = f(I) behaves in such a manner, e.g. for the D_1 line, that brightness increases 1:25 as the value of k drops from 2.0 to 1.41. /455 The number of centers changes by about 1:75 over the interval of k values covered. From the curve of k = f(I), Gouy derived a curve between brightness I and number of centers $\mathfrak{N}$ under the assumption that vapor density and layer thickness were interchangeable. Under this assumption,

$$\frac{I_{2l}}{I_l} = k = \frac{I_{2d}}{I_d}$$
$$I_{2d} = I_d \cdot k_d$$

(l = layer thickness, d = vapor density). If, on the basis of Gouy's work, we now arbitrarily set I = 1 and d = 1 for k = 1.9, then

$$I_{d=2} = I_{d=1} \cdot k_{d=1} = 1,9$$
$$I_{d=4} = I_{d=2} \cdot k_{d=2} = 1,9 \cdot k_{d=2}$$
$$= 1,9 \cdot k_{I=1,9}$$

We can take the value of k for I = 1.9 from the curve which represents k as a function of I and thus evaluate l for d = 4. We thereby obtain values of d as a function of l from the measured relationship between k and I and, since d is proportional to $|\mathfrak{N}|$, I (relative values) as a function of $|\mathfrak{N}|$. From the two functions

$$k = f(I) \quad \text{and} \quad I = g(\mathfrak{N})$$

we can now derive a relationship between k and $\mathfrak{N}$, i.e. a function $k = \phi(\mathfrak{N})$. Thus it is possible, in principle, to graphically determine, from two measured k values in each case, the ratio of particle numbers associated with these k values.

Ladenburg and Reiche have attempted to theoretically derive the dependence of LA upon brightness or the number of centers which Gouy found experimentally. LA was first calculated as a function of particle number (k = $\phi(\mathfrak{N})$) for the case in which emission and absorption power as a function of frequency obeys classical (Drude-Voight) dispersion theory, and secondly for the case in which the above-mentioned relationship is given by the Rayleight function, which gives consideration to the motion of vapor molecules (cf. [25]). For low vapor densities and thus low bright- /456 nesses, the observed values follow a curve for the Rayleigh function well, but for high brightnesses they follow the curve calculated from dispersion theory. In the calculation of spectral line brightness I as a function of the number of centers $\mathfrak{N}$ [I = g($\mathfrak{N}$)], total absorption, which experiences a continuous spectrum within the vicinity of the spectral line, was likewise obtained under the assumption of Rayleigh or dispersion distribution in the line; in addition, proportionality was assumed between emission and absorption power, as is applicable, for example, in the case of thermal radiation. Rules were found here which likewise agree

8

with Gouy's results: namely, that for a small number of centers, brightness I is proportional to number of centers $\mathfrak{N}$, but for a large number of centers, it is proportional to the root of the number of centers and attenuation ν'. In its second part, this rule was confirmed by the measurements of H. Senftleben [4], who simultaneously determined flame intensity and the number of emission centers in Na flames. It follows from the root law that in the limiting case of high numbers of centers -- at least in the case of dispersion distribution -- the gradually decreasing intensity ratio of doublet components approaches the square root of the true value. The assumption is made here that attenuation is the same for both components. The law has been confirmed for D lines in the Bunsen burner flame.

On the basis of the relationships discussed, we can thus obtain information, for one thing, as to whether large, medium or small numbers of centers are present if we simultaneously measure intensity ratio and light absorption for both components. The $k = \phi(\mathfrak{N})$ curve may also allow the ratio of particle numbers and thus the true intensity ratio $(IR)_t$ to be determined directly with the aid of the measured k values. Due to the flat shape of the above-mentioned curve, however, this determination is very imprecise and is promising only for medium k values.

3. The Flame and Its Properties

As was just shown, it is important to make the density of the luminous vapor as low as at all possible. A light source therefore /457 had to be selected which meets this requirement and also permits regulation of the number of centers within certain limits. The electric arc and other electrically excited light sources had to be eliminated from the outset. The flame, whose emission is probably based essentially on thermal radiation, has the disadvantage of low brightness for small numbers of particles. If we

wish to avoid this, we must make the temperature as high as possible. The oxyhydrogen flame was used for this reason. The second requirement, for a small layer thickness, could be satisfied by the designing of a special burner. Three small brass tubes, which must be adjustable with respect to one another, form the burner. The design can be seen from Fig. 1. The two outside tubes feed the combustible gas (hydrogen), the center tube feeds oxygen[4]. The flame obtained with this burner has a transverse layer thickness of about 10 mm. The shape of the flame can be adjusted by means of the shape and position of the nozzles.
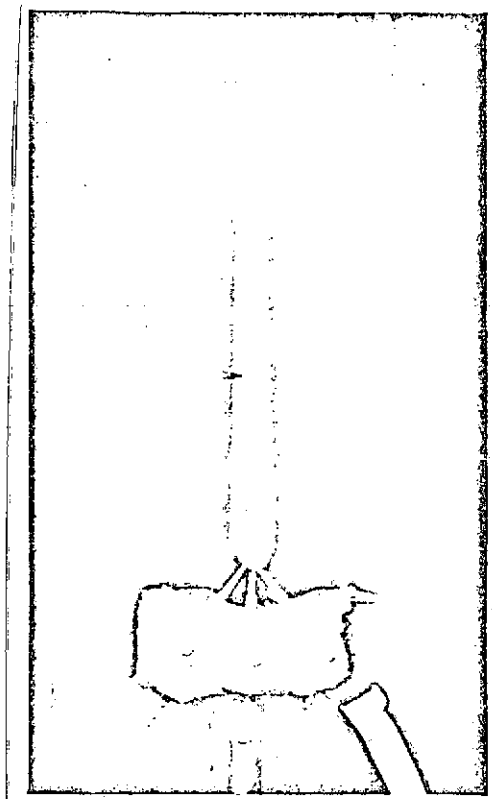
The flame was colored by feeding into it an aqueous solution of a salt of the metal to be studied, in a fine spray produced by a Regener atomizer [26]. The strength of flame coloration could be varied within wide limits by changing the concentration of the salt solution. Fig. 2 shows a diagram of the setup used for flame coloration.

Fig. 1. The arrow indicates the point in the flame used for measurement.

Flame temperature constancy, which is a condition for intensity constancy, was determined by the line reversal method [27]. However, these studies were always performed with the D lines that always appear and not with the second principal-series terms of Cs, Rb and K,

[4] The required gases were obtained from the firm of Griesheim-Elektron, which supplied the hydrogen at a special price, for which we would like to express our thanks at this point.
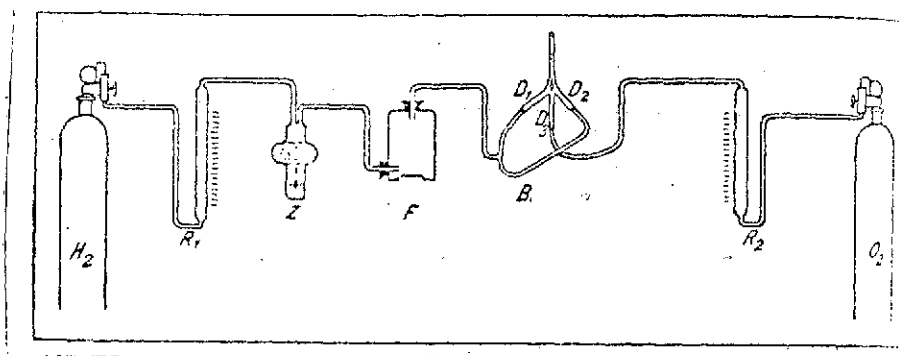
Fig. 2.

Key: R = rotameter
       Z = atomizer
       B = burner

siñce reversal measurements with these terms are extremely diffi-
cult because of the low sensitivity of the eye in the spectral
region containing these doublets.

The positive carbon cup was used as a "reversing" light source;
its intensity was attenuated with Nicol prisms and calibrated by   /458
reversal measurements of the D lines from the flame of a Méker
burner of known temperature.[5] A reversal temperature of about
2600° absolute was obtained in this manner for the oxyhydrogen
flame employed. But this determination has a precision of no
better than ±50°. The individual reversal temperatures measured
during the recording process fluctuated by ±1%. This would corres-
pond to a variation in the number of excited atoms in the flame of
about 10%. But this variation is certainly even smaller, since a
portion of the fluctuations can be blamed on small changes in
cup brightness in any case.

---

[5] This was based on the value of about 2073° absolute determined by
   H. Kohn [27] for the flame of the Méker burner. It is neverthe-
   less not certain whether the value is still valid, since the
   composition of illuminating gas has changed in the meantime.

4. The Photographic/Photometric Method

The photographic/photometric method was chosen for the study. A certain masked-off zone of the flame, always the same, was projected on the spectrograph slit, and slit width was adjusted so that no signs of intensity distribution within the lines themselves could be observed. One of the now conventional methods was used which circumvent the time-consuming photographing of intensity marks which is necessary for the production of intensity-density /459 curves, namely the absorption wedge method in a form similar to that described by T.R. Merton [28]. The absorption wedge was mounted in front of the spectrograph slit in such a manner that the refracting edge lay parallel to the plane of the slit and perpendicular to the slit. Various points along the slit are therefore associated with various thicknesses and thus also various transparencies of the wedge. The intensity at a particular point for each spectral line on the photographic plate is thus determined by the transparency of the wedge at the corresponding point on the latter. If I^0 indicates the intensity of incident radiation and I that of transmitted radiation at a point at a distance l from the vertex of the wedge, then the following relation holds:

$$I = I^0 \cdot e^{-\gamma l}. \qquad (5)$$

In order to compare the intensities I_2^0 and I_1^0 of two lines, we must locate points l_2 and l_1 of equal density in the two continuously attenuated lines on the photographic plate. The following then applies to the intensity ratio of the two lines which is being sought:

$$\frac{I_1^0}{I_1^0} = e^{\gamma(l_1 - l_1)}, \qquad (6)$$

where, for the sake of simplicity, the superscripts in I_2^O and I_1^O will be omitted below. It is assumed here that γ does not vary within the wavelength region of the two lines, i.e. within the vicinity of the closely neighboring doublet components here. Evaluation of the photographs must be preceded by calibration of the wedge, i.e. determination of gradient γ. To accomplish this, we print a series of intensity marks on one and the same plate by means of a constant-burning light source. (I used an Hg lamp[6] or a Nernst filament for this.) A rotating Lummer-Brodhun sector was /460 used to produce the marks[7]. Under the intensity marks, either the line spectrum of the Hg lamp or the continuous spectrum of the Nernst filament was photographed through the wedge with the same exposure time (Fig. 3). It was quite important here that the entire height (about 10 mm) of the spectrograph slit be uniformly exposed to the light.

The photograph obtained through the wedge is evaluated photometrically (at a given wavelength) at constant intervals in the direction of increasing wedge thickness from an arbitrary zero point, and the intensity I associated with the density S at each wedge point l is taken from the density curve obtained from the intensity marks.

If we now plot the logarithms of intensities as a function of l, we actually obtain a straight line as called for by the above equation (5) in logarithmic form:

$$\log I = \text{const} - \gamma l \cdot \log e \qquad (5a)$$

---

[6] An air-cooled Heraeus quartz lamp was employed in the case at hand. It had to be lit about an hour prior to the intended photographing so that it would be burning at constant brightness.

[7] According to measurements by A.E. Weber [29] and F. Goos [30], the rotating sector is suitable for producing the intensity marks.
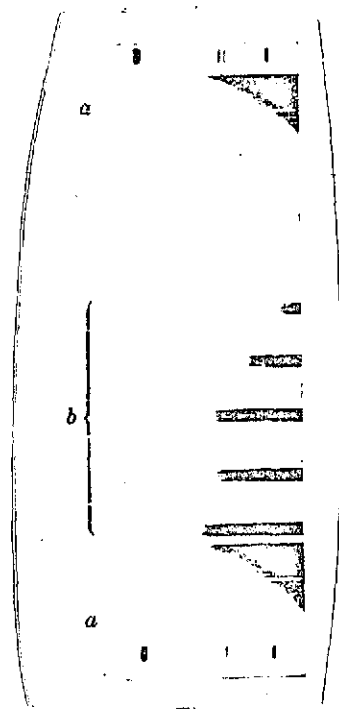
Fig. 3. A. Nernst
filament through
wedge. b. Inten-
sity marks (with
rotating sector.

The lines drawn in (Fig. 4) have been
calculated by the method of least squares.
As we see, these lines match the data quite
well. Attenuation by the Uviol wedge used
in this work was 1:11.7 for 10 mm at
λ = 436 $\mu\mu$ [sic]. Since the gradient varies
considerably with wavelength, calibration
had to be performed at all wavelengths at
which the lines were to be studied. The
values of the gradient were unaffected by
whether a line spectrum or a continuous
spectrum was used for calibration. The pre-
cision with which the gradient is deter-
mined is at least ±1%.

All photographs were measured out with
a Hartmann microphotometer which was made
available to me for all of the measure-
ments by Professor Dr. Ladenburg, for which
I would like to express my sincere thanks at this point.

In order to make microphotometric measurements unnecessary,
Merton [31] developed a method which was further extended during the
course of this work[8]. The principle of this method is the fol-
lowing: Due to absorption by the wedge placed in front of the slit,
the photographs exhibit a continuous decrease in density -- as a
function of increasing wedge thickness -- the behavior of which
is determined by the e function given in equation (5) at the
appropriate illumination level, the darkening changes to fogging;
i.e., the phenomenon, e.g. the spectral line, "ceases." As we
saw during development of the measurement method, it is important

---

[8] For reasons to be discussed later, this method may only be ap-
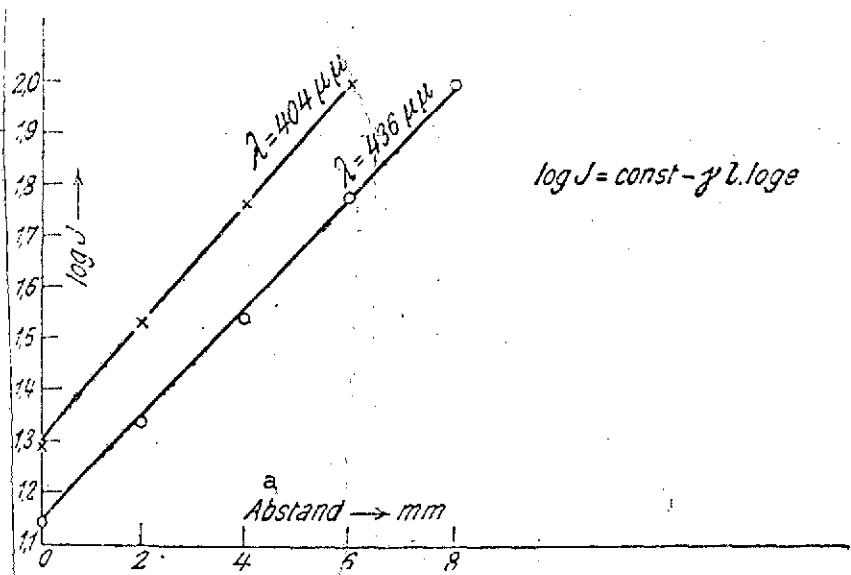plied with great caution, however (see Section 5).

Fig. 4. Curves for evaluating wedge gradient
for λ = 436 and 404 μμ.

Key: a. Distance

to determine point pairs of equal density for the lines to be com-
pared. Such a point pair is also formed, for example, by the
end point of the two components on the plate. These end points
must thus be determined. This is done in the following manner:
A contact-copy diapositive of the photograph is made, of which a /462
photographic enlargement on silver bromide paper is made through
a grid. We thereby obtain an enlarged picture of the original
photograph, but no longer continuously coherent lines but rather
rows of pointlets, corresponding to the grid openings, of gradually
decreasing density. The last point in such a row (end of line)
can easily be determined on the enlargement. The grid which I used
has 40 lines per centimeter. Enlargement was 3.24x. If we are
off by one grid point in determining the end of the line, we ob-
tain an error of 0.077 mm in the distance $l_2 - l_1$ from which we
calculate the IR of the components.

Following Merton's example [28][9], I at first likewise used a grid (cf. Figs. 5 and 5a). If the grid was tilted relative to the spectral line, asymmetry occurred (cf. Figs. 6 and 6a) which made it difficult to determine the last visible point. It therefore proved more desirable to employ a simple grate of horizontal lines[9,10]. The photographs obtained with this are shown in Figs. 7 and 7a. It can easily be seen that a tilting of the grating cannot impair length determination. The method just described can thus replace the microphotometer to a certain extent.
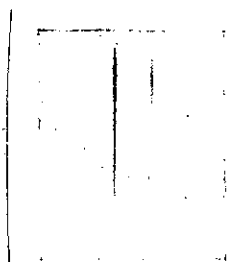

Fig. 5   Fig. 5a

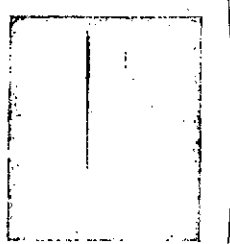Evaluation of intensity ratio of Rb doublet by "grid method".

5. Photographs and Their Evaluation

The flame zone used in photographing exhibited no appreciable differences in intensity over its entire area. Prior to the photographing, the density of the salt solution to be fed into the flame was determined with a pyknometer, and the concentration was calculated from this. After the photographing, exposure time for which varied between 1/2 min and 7 hours, the plates (Hauff extra-rapid) were developed for about 3 min in a 24% metol-hydroquinone solution. After photographing had been finished, /463 the concentration of the salt solution was redetermined. Higher densities than those prior to photographing were sometimes determined here. This phenomenon can perhaps be attributed to

---

[9] Remark added at time of printing: In a more recent article [32], Merton has likewise employed a line grating for reproductions.

[10] Both the grid and the line grating were supplied to me at no cost by the firm of Efha-Rasterwerk, Munich, for which I would like to cordially thank that company.

16

Evaluation of intensity ratio
of Rb doublet by grid/grating
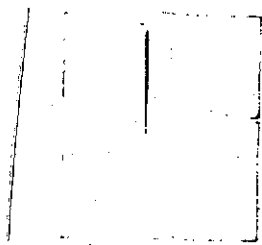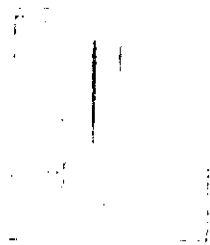method

Fig. 6   Fig. 6a

Asymmetry due to tilting of
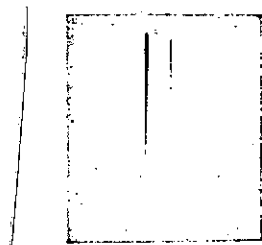grid relative to line.

Fig. 7.   Fig. 7a

Photographs made with line
grating.

contamination by the hydrogen.
Occasionally, however, these
higher densities were also
caused by actual increases in
the concentration of the salt
solution to be attributed in
any case to the atomizer's
mode of operation. At the same
time, the increase in concen-
tration was confirmed by the
fact that photographs often
exhibited considerably higher
densities than others, obtained
under otherwise equivalent
conditions, for which the solu-
tion had been made up at the
same concentration. Various
discrepancies in the first ex-
periments, which will be
discussed later and in which
densities were not yet being
checked, can perhaps be attri-
buted to this. In later

experiments, in order to be quite certain, the constancy of density
was also checked occasionally during photographing for very long
exposure times, and if an appreciable change was detected, freshly
made-up solution was introduced.

Prior to the actual evaluation of the photographs, measurements/464
across several lines were performed with the microphotometer.
Fig. 8 shows the results for the Rb doublet with a slit width of
0.1 mm. We see that density is uniform over a distance of 0.06 mm
but drops off somewhat at the edges. The two components of a
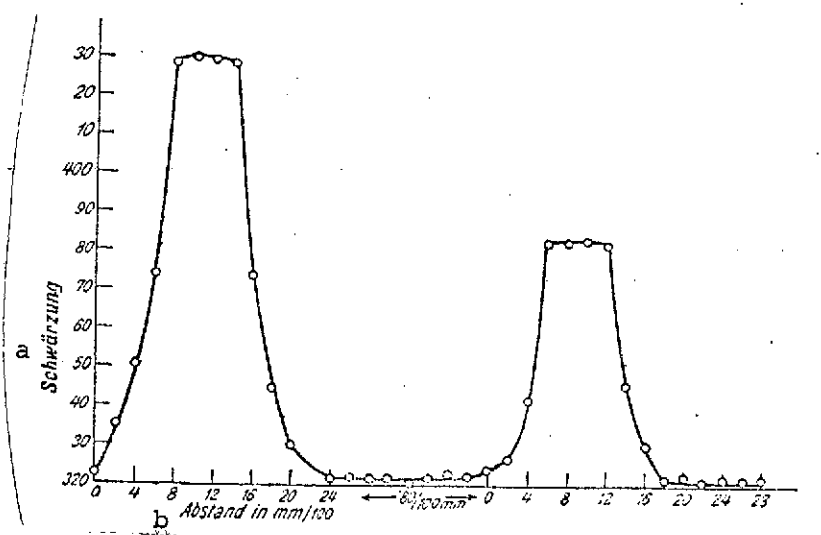doublet to be studied were now measured photometrically at equal

Fig. 8. Transverse measurements ((performed on a photograph of the Rb doublet).

Key: a. Density; b. Distance

intervals in the longitudinal direction, i.e. in the direction of decreasing density, and the density values obtained were plotted as a function of distance from the zero mark. Two parallel curves were found here, as shown in Fig. 9, whose behavior is determined by the exponential function for intensity drop along the lines. Points with equivalent ordinates correspond to equal density. Their distance is the $l_2 - l_1$ being sought. This quantity can be determined reliably thanks to the many measurement points along a line, which establish the position of the curve very precisely. Distance is probably accurate to within $\pm 1/10$ distance unit in the figure (i.e. 0.1 mm on the photograph).

The method of evaluation described above calls for photographs in which no continuous background (CB) is superimposed on the lines. In the flame spectrum, however, there is always a more or less intense CB in the spectral region under consideration here. If the flame is highly colored, this amounts to only a very small fraction of the brightness of the lines to be studied and is not at all apparent between the lines for the small exposure
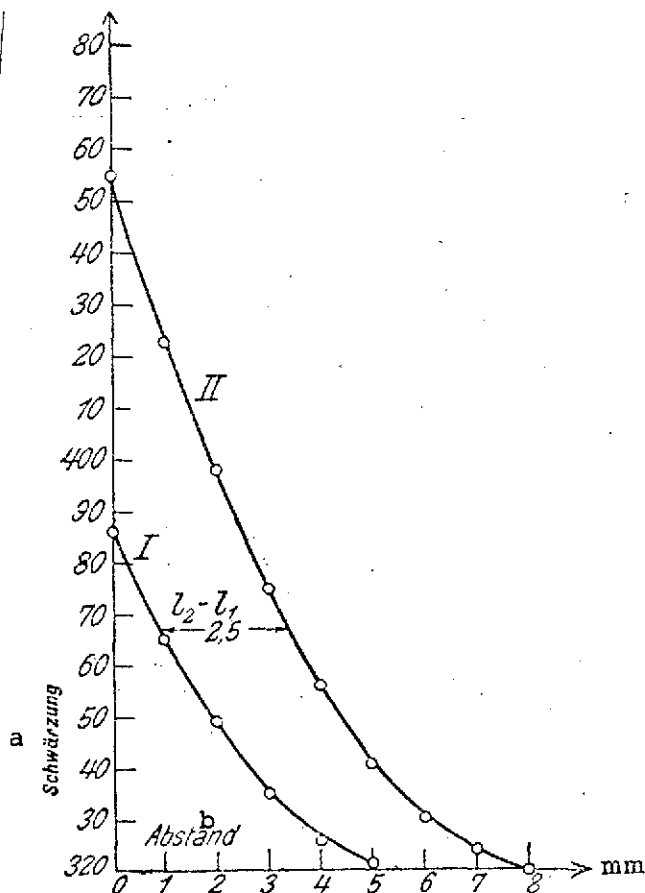
18

Fig. 9. Density along the compo-
nents of a doublet as a function
of distance from an arbitrary
zero mark (photograph of the K
doublet).

Key: a. Density; b. Distance

times which are then adequate.
In the case of weak flame
coloration, i.e. low concen-
trations of the salt solution
fed into the flame, of par-
ticular interest to us here,
the CB can amount to a con-
siderable fraction of line
brightness, however; on the
other hand, it also appears on
the plate between the doublet
components after the long
exposure times now necessary
and can be measured out here.
CB is covered by the equation

$$\frac{I_2}{I_1} = \frac{I_1' - I_k}{I_1' - I_k} = \frac{\frac{I_2'}{I_1'} - \varrho_1}{1 - \varrho_1} \qquad (7)$$

Here, the primed quantities
refer to the measured in-
tensities and the unprimed
quantities to the actual in-
tensities of the components.
In addition, $\rho_1 = I_k/I_1'$, where
I_k is the intensity of the
CB.

This formula thus permits the "actual" intensity ratio I_2/I_1
to be calculated from quantities which can be found by making
measurements on the plate. On a photograph in which a CB can be
seen, we must thus photometrically measure not only the two com-
ponents (I_2', I_1') but also the CB (I_k) from the same starting
point and in the same steps (l_k). We thereby obtain three curves /466

Fig. 10.
Key: a. Density; b. Distance

(II, I and K; for example, cf. Fig. 11) for evaluating IR. From distances $l_2' - l_1'$ and $l_1' - l_k'$, we can use the equations

$$\frac{I_2'}{I_1'} = e^{\gamma(l_2' - l_1')} \qquad (8)$$

$$\frac{I_1'}{I_k} = e^{\gamma(l_1' - l_k)} = \frac{1}{\rho_1} \qquad (9) \qquad \underline{/467}$$

to first determine the quantities I_2'/I_1' and ρ_1, from which we immediately obtain the actual IR I_2/I_1 by substituting into formula (7).

Photographs Cs 140b (Fig. 10, concentration 2%, exposure time 7 min) and Cs 138b (Fig. 11, concentration 0.5%, exposure time 20 min) will serve as examples. No CB could /468 be observed on the plate of the former photograph. IR could thus be evaluated with equation (6). On the other one, however, it was necessary to deal with a CB whose intensity amounted to 19% of the weak component. This raised the IR determined with equation (6) by about 17%.

Photographs Rb 111c (Fig. 12, concentration 2%, exposure time 1 hour) and Rb 111b (Fig. 13, concentration 0.5%, exposure time 2 hours) will serve as additional examples.

20

Fig. 11.

Key: a. Density; b. Distance

Within the figure (labels): Cs 138; 0,5 % CsNO₃; $J_2'/J_1' = 3,48$; $\varrho = 0,19$; I; II; $J_2/J_1 = 4,06$; $l_2'-l_1'$ 5,2; $l_1'-l_K$ 7,0; K; Schwärzung; Abstand; mm

Since no CB could be observed in the former, IR could be determined directly with equation (6). The second photograph indicates quite clearly how cautiously we must act in taking CB into consideration. The CB, which is hardly visible on the plate of this photograph, increases the ratio (I_2'/I_1') obtained directly by measuring the components by about 13%, i.e. from 1.80 to 2.06. As can be seen from curves I and II, the two components have a "length" of 7.5 and 9.5 mm, respectively. (The density value "320" indicates fogging.) If they had come out shorter by 2 mm for a somewhat shorter exposure time, the region of darkening into which they fall would still be relatively favorable; there would also be enough measurement points for a good evaluation. But the CB would no longer be detectable on the plate at all, and we would consider the IR determined directly from curves I and II with equation (6) to be the actual value, i.e. we would have obtained a result involving an error of about 13%.

Fig. 12.
Key: a. Density; b. Distance

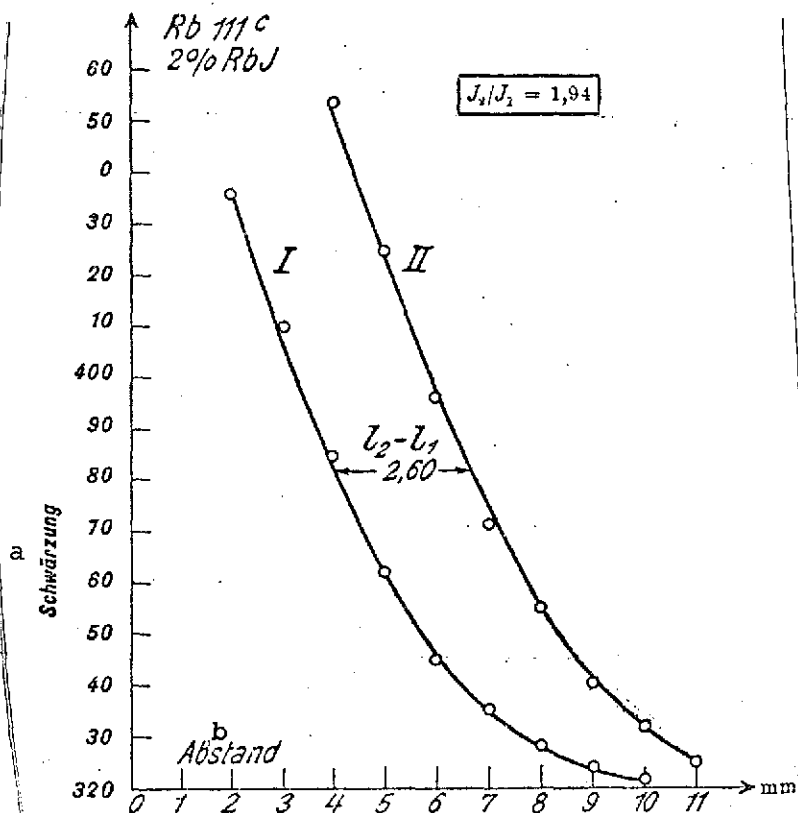We shall consider /470 the following in order to make a general estimate of error: It can be seen from formula (7) that the quantity $\rho_1 = I_1'/I_k$ is decisive for a given deviation δ (in percent) of the directly measured value I_2'/I_1' from the actual value I_2/I_1; ρ_1 itself determines the distance $x = l_1' - l_k$. Thus the "length" of the weak component (curve I) must be $\geq$ x mm so that the background ($I_k = \rho_1 \cdot J_1$) can be determined and taken into consideration[11].

If curve I is at least x mm long and no background is perceivable, then although we cannot state that none is present at all, we can still conclude that it amounts to less than the fraction ρ_1 of I_1 corresponding to the value x and that any correction which might have to be applied does not exceed the value δ associated with the particular ρ_1. The values of x for given values of δ and ρ_1 have been calculated in tables, not reproduced here, for a number of values of the ratio I_2'/I_1' within the interval within which it lay in the observations to be discussed later. The calculations had to be made separately for the measurements performed on the three doublets, since the wedge gradient differs in

---

[11] The greater the wedge gradient is, the shorter x of course is.

Fig. 13.
Key: a. Density; b. Distance
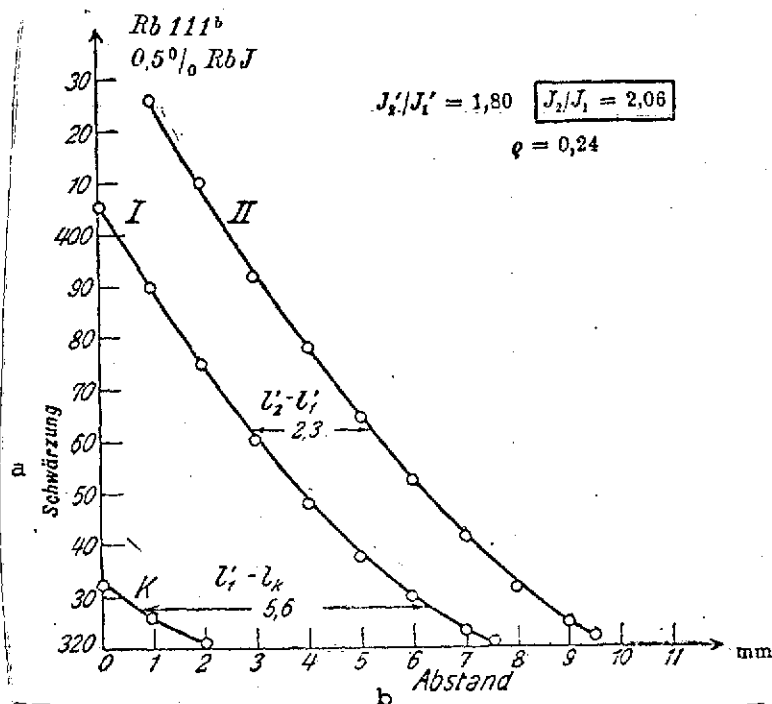
the spectral zones of the lines mentioned. The tables thus provide information as to how large the values of x must be in order that for a given measured ratio I_2'/I_1', the correction which might have to be applied as the result of a suppressed CB does not exceed the quantity δ. The above-mentioned tables could be used to arrive at a decision as to how much exposure is needed for any CB that is present to be brought out and measured reliably. If no CB can be seen on a photograph, it is first necessary to determine how far the weak component I_1 reaches, and we can then use the tables to give the upper limit under which the increase due to the CB not apparent on the plate is certain to remain. In the case of strong flame coloration and a gap which is not too wide, in which CB in any case amounts to a quite insignificant fraction of I_1, this discussion need not be applied. We would set the limit of error indicated by it too high here. /471

Due to CB, the "grating method" which Merton and I have described must also be applied with a great deal of caution. Since it is precisely the ends of the lines which we wish to have on the plate, we must keep their length relatively short. In order to bring out a CB which in relative terms is not too strong or to be

able to estimate its magnitude to some degree in accordance with the above considerations, we must thus work with steep wedge gradients here. In all cases, we must first be very careful to ascertain whether there is a CB on the original plate and, if so, whether it is reproduced on the copies well enough to be properly measured. If we observe the above-described precautionary measures, however, there is nothing to be said against application of the grating method, since its precision is otherwise not inferior to measurement with the microphotometer.

These measurement methods just described are only applicable in this form if we can consider the sensitivity of the photographic plates to be equal at both components of each doublet, an assumption which has been made use of here (cf. [33] in this regard).

6. Experimental Setup for Simultaneously Measuring Intensity Ratio and Line Absorption

The simultaneous measurement of IR and line absorption had to be done by the reflection method described by Gouy [7], since two identical flames could not be produced. The experimental setup was designed in such a manner that the lines from the unreflected flame, i.e. from a single layer, and those from a layer doubled by reflection could be photographed simultaneously on the plate. For this purpose (Fig. 14), the flame was enclosed between two stops (B_1, B_2), of which that facing the spectrograph (B_1) was projected on the spectrograph slit by lens L. The masked-off portion of the flame had to be taken large enough that the slit was illumi- /472 nated quite uniformly over its entire height for good "filling" of the spectrograph. The height of the front stop was 18 mm, its width was about 4 mm. Lens L projected a somewhat reduced image of it on the slit. The rear stop had to be large enough that the image of it produced by the concave mirror H which was used had the dimensions of the front stop. This size, as well as the necessary distance between the two stops (42 mm) was found by means
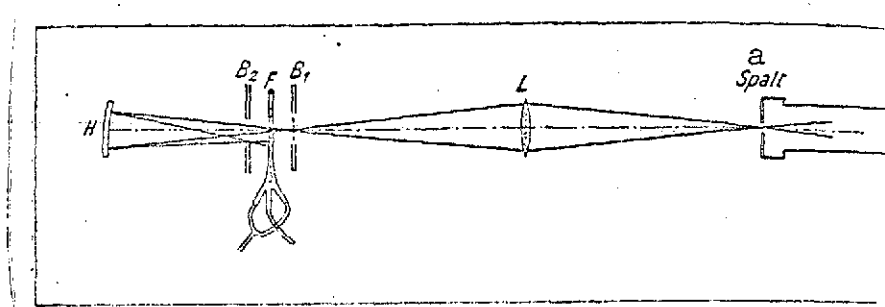
Fig. 14

Key: a. Slit

of a scale drawing. The rear stop was first projected into the
front stop by the concave mirror. This means, however,-- as one
can easily demonstrate graphically -- that all light from flame F
which fell on the rear stop was returned through the flame by the
concave mirror, and the entire front stop was uniformly filled
with this light. Aside from losses due to the mirror's reflectivity,
the spectrograph slit was also thereby filled with light from the
double flame layer. (The consideration of reflectivity will be
discussed further below.) It was necessary, however, that radia-
tion from the single layer and that from the layer enlarged by
reflection be photographed simultaneously. This was achieved in
the following manner: The concave mirror was inclined just
slightly relative to the axis of the beam path, so that the image
of the rear stop covered only half of the front stop. Conse-
quently, radiation from the single layer fell on one half of the
spectrograph slit and that from the layer enlarged by reflection
fell on the other half. The boundary between the two halves could /473
be seen in the form of a sharp edge if carefully adjusted on the
slit. The same method for measuring k values and IR as described
above was applied, namely the absorption wedge method.

With the setup described above, a line on the photograph
(for example, see Figs. 15a and 16a) now no longer exhibits a
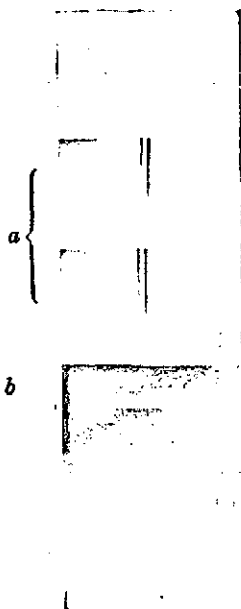continuous decrease in density over its entire length, but rather

25

Fig.15. a. Photographs of the Rb doublet. b. Photograph for determining the reflectivity of the mirror at the Rb lines.

makes a jump beyond the boundary edge, i.e. at the point at which radiation from the double layer begins, density suddenly jumps to a higher value. The photographs are evaluated and the material plotted on graph paper in the manner described in Section 5.

Let us refer to Fig. 17 for a more detailed explanation; the curves represent the results from a photograph of a flame colored with a 2% RbI solution.

Curves I and II show the dropoff in density in those parts of the components which correspond to radiation from the single layer; they are thus obtained by photometrically measuring the upper halves of the components. At wedge point 5, i.e. 5 mm from the point at which measurement begins, the curves break off suddenly, to begin again at wedge point 6 with larger ordinates, i.e. greater density. These curve segments ($\overline{I}$ and $\overline{II}$) correspond to the parts of the components which are due to radiation from the double layer. Curve K was obtained by measuring the CB between curves I and II.

By suitably choosing the starting point for measurements (zero point) we kept the last measurement point on the unreflected component from coming too close to the boundary, since it was thereby easy to measure too high a density for this point, resulting in error in evaluation of the curves.

If no CB exists, the curves obtained are evaluated (see above) by the following formulas
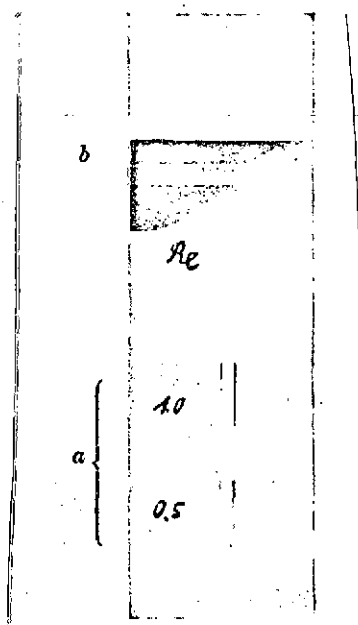
Fig. 16. a. Photographs of the Cs doublet. b. Photograph for determining the *reflec-tivity* of the mirror at the Cs lines.

$$\frac{I_2}{I_1} = e^{\gamma(l_2 - l_1)} \quad \text{(single layer)} \qquad (10a)$$

$$\frac{\bar{I}_2}{\bar{I}_1} = e^{\gamma(\bar{l}_2 - \bar{l}_1)} \quad \text{(double layer)} \qquad (10b)$$

When the layer is doubled by reflection, /474 the k values are not given directly by the ratio $\bar{I}/I$; rather, the reflectivity (R) of the concave mirror must be included in the calculations. This gives the formulas

$$k_1 = \frac{\bar{I}_1}{I_1} \cdot \frac{1}{R} - \frac{1-R}{R}; \qquad k_2 = \frac{\bar{I}_2}{I_2} \cdot \frac{1}{R} - \frac{1-R}{R} . \qquad (11)$$

If CB must be taken into consideration in the photograph, the following series of formulas must be used for evaluation:

/475

$$\frac{I_2}{I_1} = \frac{\dfrac{I_2'}{I_1'} - \varrho_1}{1 - \varrho_1} \quad (I) \qquad \frac{\bar{I}_2}{I_1} = \frac{\dfrac{\bar{I}_2'}{I_1'} - \bar{\varrho}_1(1+R)}{1 - \bar{\varrho}_1(1+R)} \quad (II)$$

$$\frac{\bar{I}_1}{I_1} = \frac{\dfrac{\bar{I}_1'}{I_1'} - \varrho_1(1+R)}{1 - \varrho_1} \quad (III) \qquad \frac{\bar{I}_2}{I_2} = \frac{\dfrac{\bar{I}_2'}{I_2'} - \varrho_2(1+R)}{1 - \varrho_2} \quad (IV)$$

$$k_1 = \frac{\bar{I}_1}{I_1} \cdot \frac{1}{R} - \frac{1-R}{R} \quad (V)$$

$$k_2 = \frac{\bar{I}_2}{I_2} \cdot \frac{1}{R} - \frac{1-R}{R} . \quad (VI)$$

In these formulas, the ratios obtained from the primed I values are intensity ratios in which CB is not yet taken into consideration. The overbar labels those intensities obtained by reflection; the quantities ρ_1, ρ_2 and $\bar{\rho}_1$ have the following respective meanings:

$$\frac{I_1'}{I_k'}, \quad \frac{I_2'}{I_k'} \quad \text{and} \quad \frac{\bar{I}_1'}{I_k'} .$$

27
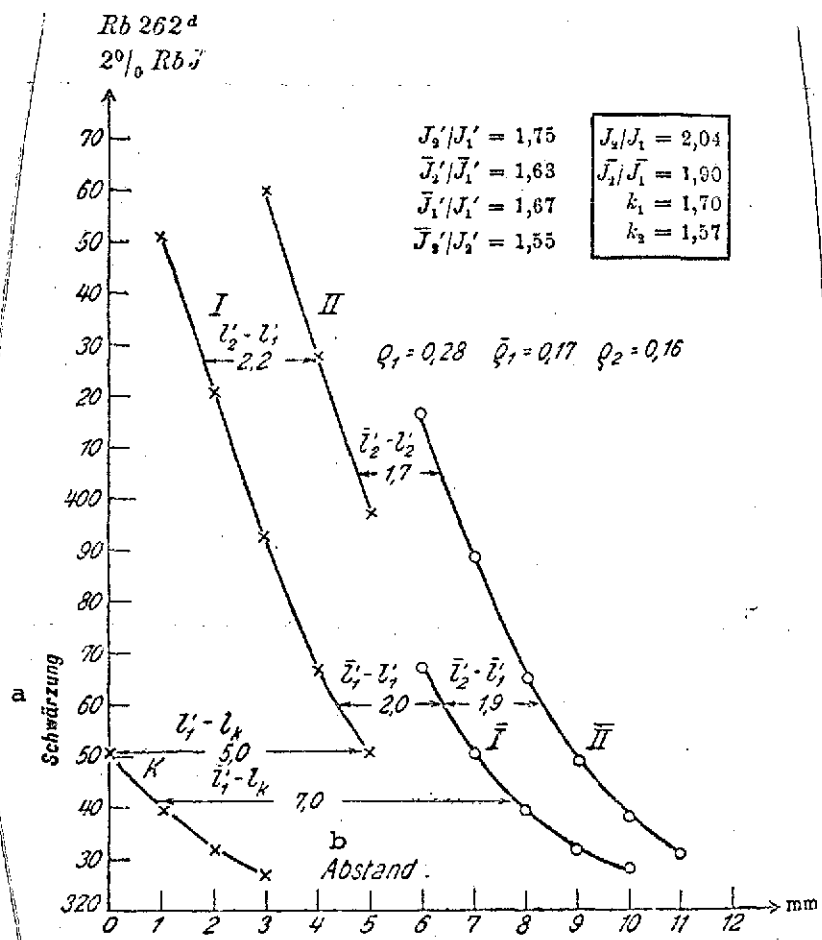
Fig. 17.

Key: a. Density; b. Distance

Since the reflectivity R of the concave mirror appears in all
formulas except (I), evaluation of the curves requires the measure-
ment of R. It was measured with a bright illuminating gas flame
which was lit in the oxyhydrogen flame burner by feeding
illuminating gas to the two outside nozzles in place of hydrogen.
Only enough oxygen was added to maintain the flame. As a result,
the upper third of the flame burned brightly. This portion of the
flame was now photographed through the wedge in exactly the same
manner as the oxyhydrogen flame, so that a continuous spectrum
was obtained in the photograph (Figs. 15b, 16b) whose upper portion
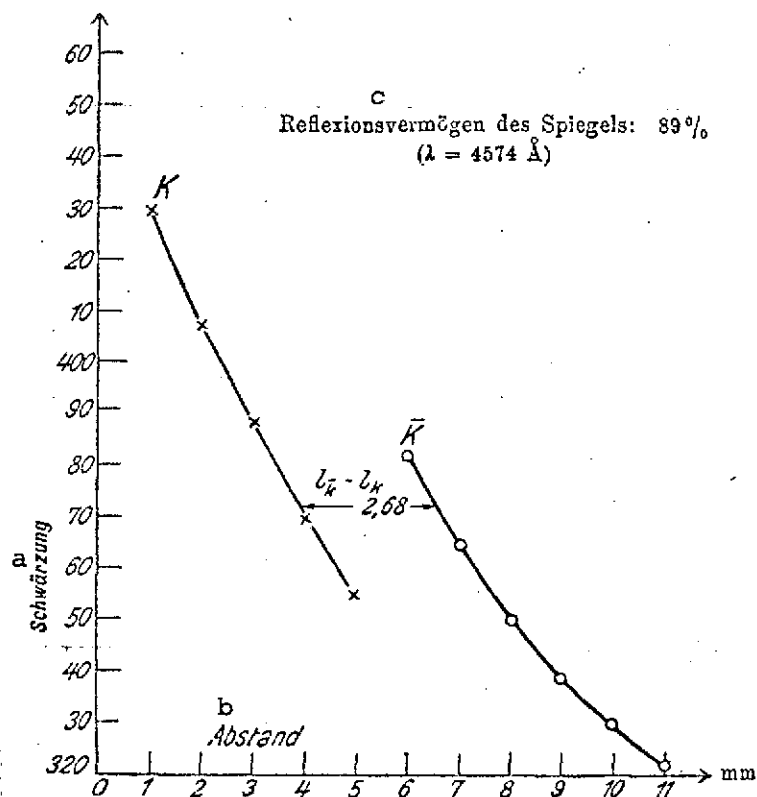
Fig. 18.

Key: a. Density; b. Distance; c. Reflectivity of mirror

came from the light of the single layer of flame and whose lower portion came from that enlarged by reflection. This continuous spectrum was now measured at the wavelengths under consideration here just as the line photographs were, and graphs like those shown in Figs. 18 and 19 were obtained. In these photographs, curve K is associated with the single layer of flame and $\bar{K}$ with the double layer. By evaluating the intensity ratio $\bar{K}/K$ with formula (6), we find R directly. It has /476 been assumed here, though, that the brightness of the flame has been doubled by reflection. This would mean, however, that the flame neither scatters nor absorbs the reflected light passing through it appreciably, an assumption which is supported both by my own measurements[2] and by earlier observations by H. Senftleben and R. Benedict.

[2] We performed an ocular measurement of flame absorption using a König-Martens photometer. The illuminating flame is relatively weak, and thus measurement precision is very low ((±5%) at the Cs and Rb lines, where the eye is very insensitive. It was not possible to perceive any light attenuation by the illuminating flame which exceeds this limit.

Fig. 19.

Key: a. Density; b. Distance;
c. Reflectivity of mirror

and E. Benedikt[13]. The /477 reflection measurements were at the same time a criterion for proper adjustment of the stops. For the photographs to be discussed later, a photograph was made on almost every plate to check reflectivity. The mean value of R was 87 ± 3% for λ = 4216/02 A (Rb doublet) and 89 ± 3% for λ = 4555/9:3 A (Cs doublet). These averages agree well /478 with those given in the literature.[14]

Prior to a discussion of the results, the limits of error of the method will be discussed; only the error introduced into the results by the measurement of density and the manner in which the curves are evaluated will be covered, but not the possible error which can result from improper evaluation of the CB and which was discussed in detail in Section 5. Precision in microphotometer settings is about 3 or 4 units in

---

[13] These observations were not published. Dr. H. Senftleben was generous enough to inform me that no absorption could be measured in luminous illuminating gas flames, quite in contrast to the observations made by the same two authors [34] with the flame of the Hefner lamp, in which considerable absorption was seen (at λ = 500 μμ, for example, 21.8%).

[14] Cf. the data in Landolt-Börnstein's tables, pp. 902 ff.

30

the figures given for density. In the first measurements, in which light absorption was not yet measured, about 6 or 8 measured points were available for constructing each curve. The deviations are thereby evened out so much that the position of the curves relative to the zero point for the measurements is known on the average, in any case, to ±0.1 mm, i.e. ±1 mm on the scale of the original drawing. In the measurements which also contain data on light absorption, not so many measured points are available because of the division of the slit between radiations from the single and the double layers, as discussed above. On the average, no more than three points (sometimes even fewer) are involved in each curve). Nevertheless, the limits of error will probably still be set too high if we assume the curves to have a precision of ±0.2 mm. The distance between each pair of curves used to determine the intensity ratio would thus involve an error of 0.4 mm in the least favorable case.

In the example of the Cs 272b photograph (Fig. 20), a change in the distance between curves I and II by ±2 mm means a change in the I_2'/I_1' value of ±4 1/2%. For the various ρ values in this photograph, a change in the distance between curves of ±2 mm results in a limit of error of ±3%. These two errors can be additive in the least favorable case. The maximum possible error is thus ±8%, an error which probably will never actually occur, however. As far as the precision in evaluation of the k /479 values (formulas III-VI) is concerned, correction with the CB plays only a subordinate role in it, as one can see from Fig. 20. Intensity ratios $\overline{I}_1/I_1$, $\overline{I}_2/I_2$ are thus determined with a precision of about ±3%, just as are $\overline{I}_1'/I_1'$ and $\overline{I}_2'/I_2'$. However, reflectivity, which is probably known to within about 5%, is also involved in the k values. The figures of 8% must thus also be considered the limit of error for the k values.

Cs 272^b

1,0 % $CsNO_3$

$J_2'/J_1' = 2,68$
$\bar{J}_2'/\bar{J}_1' = 2,61$
$\bar{J}_1'/J_1' = 1,89$
$\bar{J}_2'/J_2' = 1,82$

$\varrho_1 = 0,41$
$\bar{\varrho}_1 = 0,22$
$\varrho_2 = 0,16$

$J_2/J_1 = 3,82$
$\bar{J}_2/\bar{J}_1 = 3,78$
$k_1 = 1,98$
$k_2 = 1,91$

(a) Schwärzung

II

I

II

$\bar{l}_2' - l_1'$ 4,1 — $\bar{l}_2' - l_2'$ 2,5

$l_1' - l_k$ 3,7 — $\bar{l}_1' - l_1'$ 2,65 — $\bar{l}_2' - l_1'$ 4,0
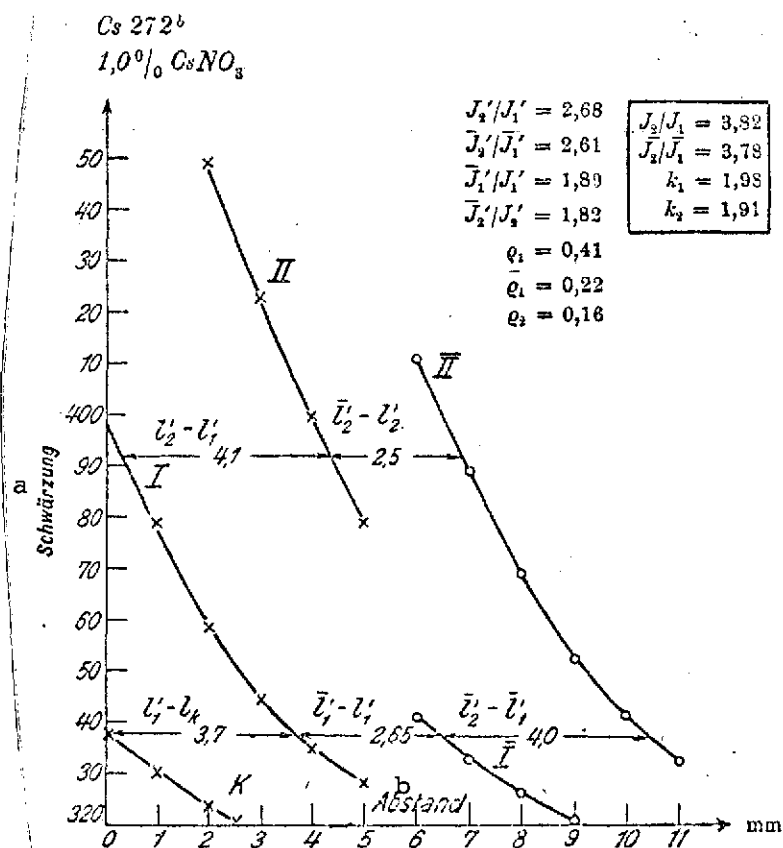
I

K

(b) Abstand

mm

Fig. 20.

Key: a. Density; b. Distance

7. Results

The results of this work will be discussed in two groups. The first contains results from the measurements which were performed without taking absorption into consideration. The second includes the results of simultaneous measurements of IR and LA.

Group I

It was shown in Section 5 that an exposure time which produces sufficient density for photometry is still inadequate and leads to erroneous results if it does not bring out the CB at the frequencies of the lines well enough to be measured. It was actually found that the first photographs, which were reported on at that time [20], were almost all underexposed in this sense, so in many cases the correction due to a CB not observable on the plate could still be considerable. The IR of the Rb doublet components appeared at that time to have reached a constant upper limit, namely 2.0, below a certain concentration of the salt solution fed into the flame. The later trials (cf. the tables below), in which the necessary exposure times were used, showed a small further increase in the IR with decreasing concentration, however, which had been hidden in the first trials.

32

In the case of Cs, the inadequate exposure time resulted in quite an erroneous result.

a) Potassium Measurements

TABLE 1

$[1s - 3p_1, p_2 \quad \lambda = 4047/4044 \text{ Å}]$			
Plate No.	Conc. of salt solution in %	$\dfrac{I_2}{I_1}$	Exposure time
K 122 b	$^1/_2$	1,93	4 hr.
121	2	1,99	$1^1/_2$ „
120	4	2,02	$1^1/_2$ „
122 c	4	1,99	$^3/_4$ „
122 d	10	1,80	$^1/_4$ „

Nowhere on the photographs given in Table 1 could a CB be detected. Thus no corrections for CB could be applied to the values of I_2/I_1 reported in Column III. To be sure, we must still permit an increase of about 15% for the photographs with 1/2 and 2% solutions on the basis of the discussion in Section 5. /481 Accordingly, we can also not state with certainty whether the value of 2.0 obtained for the intensity ratio for coloration with 4% solution represents an upper limit (cf. pp. 6 ff.). The higher densities necessary for a check could not be achieved to date for technical reasons.

b) Rubidium Measurements

TABLE 2

$[1s - 3p_1, p_2 \quad \lambda = 4216/4202 \text{ Å}]$			
Plate No.	Conc. of salt solution in %	$\dfrac{I_2}{I_1}$	Exposure time
Rb 111 b*	$^1/_2$	2,06	2 hr.
110 b	2	1,97	15 Min.
111 c	2	1,94	1 hr.
111 d	4	1,92	10 Min.
112 c	4	1,95	20 „
23 b	6	1,84	8 „
23 c	8	1,80	6 „
22 b	10	1,70	5 „
22 c	10	1,76	5 „
112 e	10	1,76	10 „
114 a	20	1,82	4 „
114 b	20	1,76	2 „

In these measurements, concentration was varied between 1/2
and 20%, i.e. between 1/40 and 1 normal. A continuous background
could be measured only in one photograph (*) and was used in the
calculations there.

We can conclude from the results in this table that the in-
tensity ratio has already reached an upper limit of 2.0 for a
4% solution. It also follows from the measured densities, i.e.
the lengths of the lines on the plate (cf. p. 22) that the possible
increase in intensity ratio due to a (suppressed) CB must general-
ly be less than 15% and even less than 10% for several values in
these photographs (from 4% down). Nevertheless, a comparison
between these trials and those run later indicates that the small
number of centers for which the intensity ratio remains constant
had actually still not been reached here. The reason for this
may perhaps be sought in irregular operation of the atomizer,
with the result that changes in solution concentration are not <u>/482</u>
always accompanied by corresponding changes in the number of
particles in the flame. Trials with an atomizer designed by
Beckmann [35] are presently in progress at the Breslau Institute.

For the same reason, it is also not possible to state, on the
basis of these trials, whether a lower limit was reached.

c) Cesium Measurements

TABLE 3

$[1s - 3p_1, p_2 \quad \lambda = 4593/4555 \text{ Å}]$

Plate No.	Conc. of salt solution in %	$\dfrac{I_2}{I_1}$	Exposure time
Cs 106 *	1	4,16	30 Min.
105 *	1	4,12	30 „
138 b*	1/2	4,06	20 „
139 b	1	4,04	15 „
141 b*	1	4,10	15 „
134 c	1/2	4,04	10 „
141 c*	2	4,05	7 „
140 b	2	3,87	7 „
136 d	4	3,63	2 „
137 a	4	3,64	2 „
141 d	10	3,31	1 „
140 c	20	3,12	1/2 „

The order used here again involved increasing solution concentrations. However, a number of changes were made with photographs for which it could be concluded from illumination time and the density obtained with it that vapor density was just as high or perhaps higher than for other photographs made with higher concentrations. In the majority of photographs, a CB could be measured with a low vapor density; the corresponding correction has already been applied in the I_2/I_1 values reported. With the 2% solution, a limit on the IR of approximately 4.0 is reached here which does not change further as concentration is reduced; the mean obtained from the results from photographs for 2% down is 4.05. A distinct dropoff in the value of I_2/I_1 only begins above /483 a concentration of 4%; a value of 3.12 is reached with more concentrated solutions. As later photographs show, however, this value is still by no means a lower limit.

As the first results of my experiments became available, an article appeared by Filippov [22], who likewise measured the second principal-series term of Cs in emission, in a Bunsen flame. When he varied the density of the salt solution used to color the flame (6 to 1/4 normal), he obtained values for I_2/I_1 in the interval between 3.4 and 3.8 which increased systematically with decreasing concentration. On the basis of his studies, he suspects that a value of 4.0 is reached in an infinitely thin layer. The figure which I obtained with weak flame coloration and that determined by Roschdestwenski (loc. cit) from dispersion measurements (4.07) would agree with this value. In neither the experiments involving the second Cs principal-series terms described above nor, even less so, the corresponding ones involving the second Rb and second K terms, however, has real evidence been produced to the effect that for the highest intensity ratio values obtained so far, the number of centers is actually low enough to be called "infinitesimally small." Only in such a case can it be rigorously concluded that the maximum obtained represents the limit which indicates the true intensity ratio $(IR)_t$.

In the first experiments set up to measure light absorption, the reflectivity of the concave mirror was not initially taken into consideration in determining whether the IR varied as layer thickness was increased or whether it remained constant; it was already possible to draw certain conclusions just on the basis of these trials as to whether the true IR had been reached or not at low concentrations. The result of this series of trials was the following:

For Cs it was found that at the weakest solution concentrations (1/2% and 1%), at which the IR of the doublet components reached a value of approximately 4.0, the increase in layer thickness due to reflection causes no change in this figure. At /484 the highest concentration used in these trials, however, the intensity ratio was reduced to a value of 2.66 by reflection.

For Rb, reflection caused a drop in the IR even at the lowest solution concentrations used, from which we can concluded that the maximum given in the preceding section still does not represent the limit for an infinitely small number of centers in any case.

We now come to the results of the final measurements, in which the magnitude of line absorption (k value) was evaluated simul- /485 taneously with the intensity ratio using the two components, taking the reflectivity of the mirror into consideration.

The method of representation used for the photographs employed in this evaluation has already been discussed on p. 26, referring to Fig. 17.

Figs. 21 and 22 and Figs. 21a and 22a show such photographs for the Cs and Rb doublets. The curves in Figs. 21 and 22 were
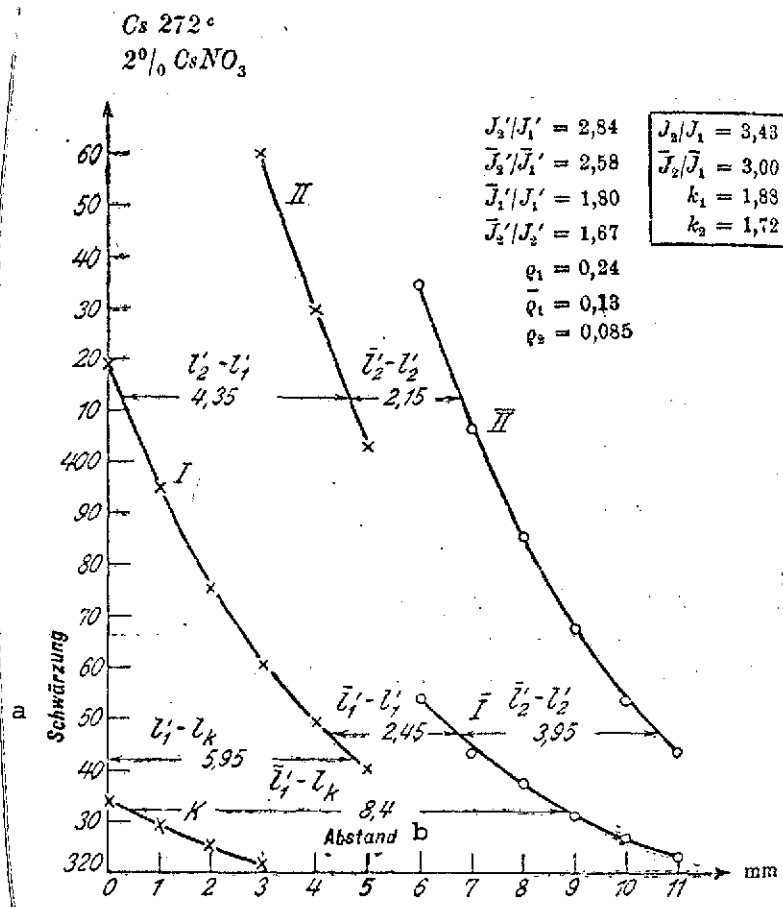
Fig. 21.

Key: a. Density; b. Distance

obtained directly by plotting the measured densities, whereas the correction for con- /486 tinuous background and reflectivity have already been applied in Figs. 21a and 22a.

It can immediately be⹊ seen from the curves that the intensity ratio of the components cannot be 2:1, for in this case the ratio of the numbers of center $|\mathfrak{N}_2 : \mathfrak{N}_1|$ would have to be 2 likewise, according to the relationships discussed previously and -- assuming the validity of Beer's law, demonstrated for D light -- the doubling of layer thickness would have to cause the intensity of the weak component from the double layer /487 to be equal to that of the strong one from the single layer.

Thus in our graph, curve II would have to form⹊an extension of curve $\bar{\mathrm{I}}$. This is not at all the case for Cs, and for Rb, too, there is a noticeable difference in the distance between curves I and II and that between curves I and $\bar{\mathrm{I}}$ and curves II and $\overline{\mathrm{II}}$.

The results of calculations for the second Cs and second Rb principal-series doublets are compiled in Tables 4 and 5.
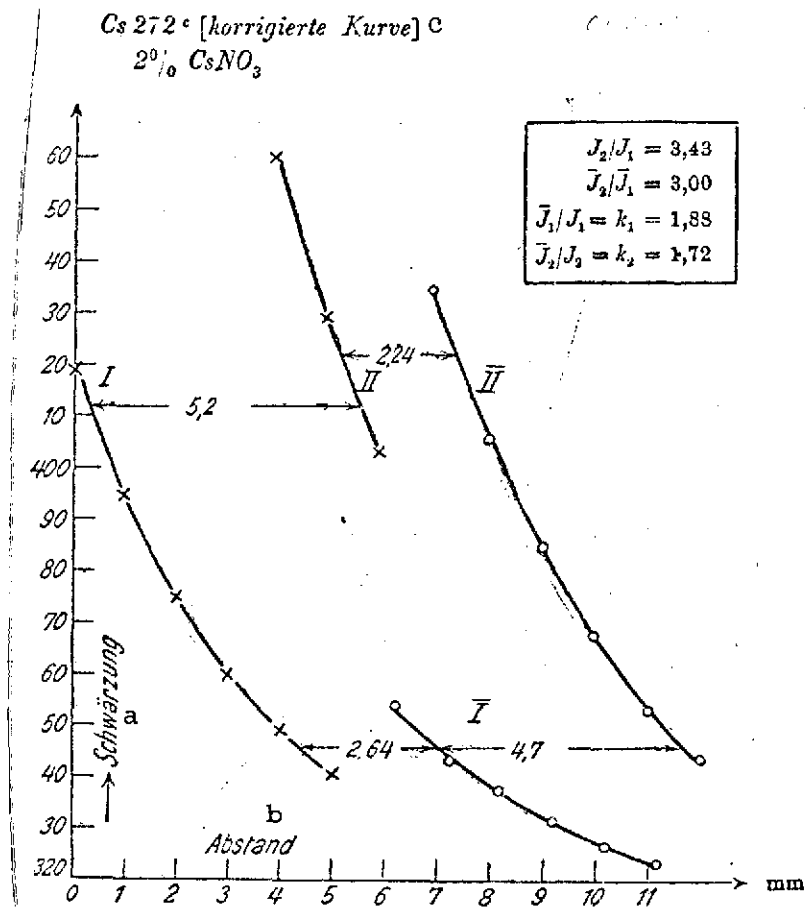
Fig. 21a.

Key: a. Density; b. Distance
        c. Corrected curve

The tables contain the photograph number in the first column, the intensity ratios for single and double layers in the second and third, the ratio of the two intensity ratios relative to one another in the fourth, the k values for the two doublet compo≑ nents in the fifth and sixth, and the ratio of the k values in the seventh. The percentage concentration of the added salt solution and the exposure time are given in the last two columns. The ratios in columns 4 and 7 should, strictly speaking, be equal, since

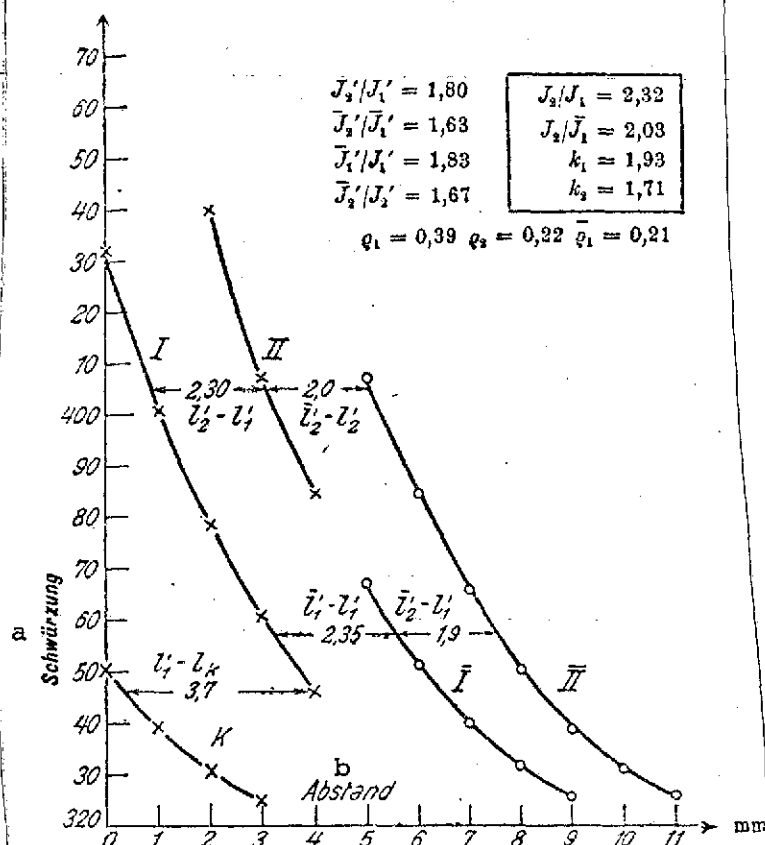$$\frac{V}{\bar{V}} = \frac{I_2}{I_1} \cdot \frac{\bar{I_1}}{\bar{I_2}} = \frac{k_1}{k_2}.$$

Fig. 22.

Key: a. Density;   b. Distance

The actual degree of agreement between the two ratios, determined independently of one another, is something of a criterion for the quality of the particular photographs. For the results reported here, deviations lie within the limit of error indicated for determination of the intensity ratio and k values. Since the evaluation of the intensity ratios is generally the more precise, due to the larger number of usable data points, more weight should be placed on the ratio $V/\overline{V}$ than on k_1/k_2. This is of definite importance in an attempt to evaluate "true" IR from the Gouy curve $k = \phi\left|(\mathfrak{R})\right|$.

a) Cesium

It can be seen from the first three photographs in Table 4, which contains those for Cs, that an upper limit for the IR was reached, and thus the number of centers is "infinitely small." This is supported not only by the constancy of I_2/I_1 (within the limit of error) and the fact that reflection did not lower the IR value, but also by the high values of k_1 and k_2; they approach a

Fig. 22a.

Key: a. Density; b. Distance; c. Corrected curve

TABLE 4

			[$\lambda = 4593/4555$ Å]					
Plate No.	$\frac{I_2}{I_1} = V$	$\frac{\bar{I}_2}{\bar{I}_1} = \bar{V}$	$V/\bar{V}$	k_1	k_2	k_1/k_2	%	Exp. time Min.
Cs 271a*	4,05	4,07	1,01 (≈1)	1,95	1,91	1,02 (≈1)	½	25
272a*	3,86	3,80	1,02 (≈1)	1,95	1,90	1,025 (≈1)	½	25
272b*	3,82	3,73	1,01 (≈1)	1,98	1,91	1,04 (≈1)	1	20
272c*	3,43	3,00	1,14	1,88	1,72	1,10	2	10
268c	3,16	2,77	1,15	1,86	1,66	1,12	4	5
270c	2,94	2,67	1,10	1,84	1,66	1,11	4	5
268d	3,01	2,76	1,09	1,81	1,64	1,10	6	3
269d	2,94	2,70	1,08	1,77	1,62	1,09	8	2
274c	2,80	2,60	1,08	1,70	1,57	1,08	10	1
269c	2,74	2,55	1,07	1,70	1,57	1,08	10	1

limit of 2 and are in agreement within the limit of error. The mean value for the ratio is

$$\frac{I_2}{I_1} = \frac{\bar{I}_2}{\bar{I}_1} = 3{,}90 \, (\approx 4{,}0).$$

The accuracy of $(IR)_t$ is strongly influenced by the presence of and consideration given to the CB, which has relatively high values precisely in those photographs made with low vapor density. For this reason, Filippov [22], for example, completely dispensed with making photographs at such low vapor densities as were studied in this work. Nevertheless, it does not appear unjustifiable to use the photographs in this discussion. In a series of photographs which were made with the same concentration of the coloring solution, the value of the continuous background relative to the weak component, i.e. the quantity ρ_1, exhibited very pronounced variations from one photograph to another. These differences in ρ_1 (ρ_1 = 0.19 to 0.65) can in any case be attributed to differences in the nature of the hydrogen used to feed the flame. Nevertheless, the same value for the intensity ratio was obtained (within the limit of error) from all photographs.

The other photographs in Table 4 decrease systematically both in IR values and in k values with increasing concentration. Where no CB could be observed and included in the calculations, increases of 10 to 15% in the values are conceivable. But even then, all of these values lie considerably below 4.0. The lowest value obtained for $\bar{I}_2/\bar{I}_1$ is 2.55, corresponding to a k_2 amounting to 1.5%, i.e. 43% line absorption. New measurements by Filippov [36] for the second Cs principal-series term in a Geissler tube even yield values for I_2/I_1 which are less than 1 for high vapor densities, something that could be attributed to strong self-reversal.

b) Rubidium

The intensity ratio values given in Table 5 decrease systematically with increasing solution concentration. Even at

TABLE 5

Plate No.	$\dfrac{I_2}{I_1} = V$	$\dfrac{\bar{I}_2}{\bar{I}_1} = \bar{V}$	$V/\bar{V}$	k_1	k_2	k_1/k_2	%	Exp. time
Rb 276*	2,32	2,03	1,14	1,93	1,71	1,13	1/2	3 hr
262 c*	2,21	1,98	1,11	1,81	1,66	1,09	1	1 hr
263 d*	2,15	1,96	1,10	1,81	1,64	1,10	1	1 1/2 ,,
263 a*	2,16	2,00	1,08	1,80	1,64	1,10	2	3/4 ,,
262 d*	2,04	1,90	1,07	1,70	1,57	1,08	2	35 Min .
264 a*	1,99	1,83	1,09	1,71	1,57	1,09	4	25 ,,
260 a*	1,99	1,80	1,10	1,70	1,52	1,12	4	35 ,,
261 b	1,89	1,77	1,07	1,66	1,55	1,07	8	10 ,,
264 c	1,80	1,68	1,07	1,60	1,49	1,07	8	10 ,,
261 c	1,71	1,58	1,08	1,62	1,49	1,09	10	10 ,,
265 b	1,75	1,67	1,05	1,63	1,54	1,06	10	5 ,,
275 b	1,71	1,58	1,08	1,58	1,45	1,09	10	5 ,,

the lowest concentration, it can clearly be seen that an upper limit has not yet been reached here (cf. the discussion of Table 2, p. 34), in contrast to Cs.

An IR value of 1.58 and a k_2 value of 1.45 are reached at the strongest concentration. This is the limit which, within the limit of error, would be expected on the basis of Gouy's measurements [7] and theory. Whether or not we are really dealing with a lower limit for I_2/I_1 and k could not be checked, since a further increase in solution concentration was not feasible.

8. Summarizing Discussion of the Results from Section 7

a) The measured results for intensity ratios and light absorption reported in the tables and discussed indicate that the highest figure so far observed (2.33) for the intensity ratio of the components of the second principal-series doublet for Rb still does not represent an upper limit. (IR)$_t$ is thus probably still greater than 2.33. For the corresponding Cs term[15], on the other

---

[15] This value is confirmed by measurements made by C.F. Hagenow and A. Ll. Hughes in the Bunsen flame [37].

hand, an upper limit and thus $(IR)_t$ appears to have been reached at a value approaching 4.0, as can be concluded both from the light absorption measurements and from a comparison of the IR /491 values for single and double vapor layers. The precision achieved so far (±6%), still quite low, does not yet allow an exact value to be given for $(IR)_t$. It can be stated with certainty, however, that this value far exceeds the 2.0 to be expected on the basis of Burger-Dorgelo intensity rule III.

It has not yet been possible to perform light absorption measurements with the second potassium term. Thus we do not yet have final evidence of whether the maximum of approximately 2.0 reported in Section 7, p. 32, corresponds to $(IR)_t$[16].

The general relationships between I and $|\mathfrak{R}|$ and k and $|\mathfrak{R}|$ given above (pp. 6)ff) likewise permit certain extrapolations to the value of $(IR)_t$. In the case of Rb, we obtain 2.5 by squaring (cf. p. 42) the smallest measured IR value of 1.58, corresonding to $k_2 = 1.45$. Since k_2 is no longer far from the lower limit $1.41 = \sqrt{2}$, this value of 2.5 (assuming the validity of the relationship between I and $|\mathfrak{R}|$ based on dispersion theory) is probably a good approximation for the true intensity ratio. Roschdestwenski [9] obtained a value of 2.57 by measuring anomalous dispersion with the Rb doublet under consideration; Gouy [7] extrapolated a value of 2.9 for the "true" IR from his intensity measurements.

The value of 6.5 for the second Cs term obtained from the smallest measured value for IR by squaring probably exceeds the value for $(IR)_t$, however, since k_2 has just reached 1.57 here.

────────────────────────

[16] However, cf. the article by A. Prokofiyev [12] referred to on p. 4 and the article just cited [37] on p. 42 by C.F. Hagenow and A. Ll. Hughes.

b) In an attempt to determine $(IR)_t$ or the ratio $\left|\mathfrak{N}_2/\mathfrak{N}_1\right|$ from Gouy's curve $k = \phi\ (\mathfrak{N})$ with the aid of the measured k values, we can either apply directly measured quantities k_1, k_2 to the curve or we can -- perhaps more accurately -- calculate k_2 from /492 k_1 with the aid of the values for $N/\overline{V}$ given in Tables 4 and 5 and make use of the pairs k_1,k_2 so obtained in further calculations. For the k values which lie near the upper or lower limits, this determination of $(IR)_t$ is of no use for the as yet relatively low measurement precision for line absorption indicated above, for such a large change in $\mathfrak{N}$ is associated with a small change in k that any ratio $\left|\mathfrak{N}_2/\mathfrak{N}_1\right|$ could be obtained. The calculations were thus performed only for the central k values (about k = 1.80 to 1.55).

In this way, we obtain values between 1.9 and 2.6 for the second Rb term; for Cs, on the other hand, we obtain figures which, while all lying above 2.0, are considerably smaller than the correctly measured $(IR)_t$. Since a relatively small change in k, still within the limit of error, practically eliminates this deviation, however, it cannot yet be decided whether the discrepancy is due to imprecision in our k measurements or whether Gouy's curve or the intensity distribution within the line assumed for computing it is invalid here.

c) It thus follows from the observed deviations from Burger-Dorgelo intensity rule III that transition probabilities for the two components of the second principal-series terms of Rb and Cs are unequal, at least in the oxyhydrogen flame; i.e.,

$$\left|a_{3p_2 \to 1s} \neq a_{3p_1 \to 1s}\right|$$

It has been assumed here, however, that "natural excitation" is taking place, an assumption which will have to be checked

in special experiments[17]. It would be premature, though, to draw conclusions from this before additional experimental material is available. Pertinent work is underway in the Breslau Institute.

9. Summary and Conclusion

The intensity ratios between components of the second prin- /493 cipal-series doublets of potassium, rubidium and cesium were measured as a function of vapor density in the hottest possible flames by Merton's photographic/photometric method. An oxy-hydrogen flame of the smallest possible thickness was used for the purpose.

Values between 1.80 and 2.02 were found for K.

The "grid method" described by Merton was improved and its applicability checked and discussed.

Line absorption was also measured for the second principal-series terms of rubidium and cesium, using a method by Gouy, in order to determine the intensity ratios of the components for an infinitely small number of centers ("true" intensity ratio). The following results were obtained:

The "true" intensity ratio of the components of the second cesium principal-series terms has an approximate value of 4.0 in the oxyhydrogen flame.

In the case of rubidium, it was not yet possible to reach the value for the "true" intensity ratio of components of the second principal-series term. It is definitely greater than 2.3, however. These results clearly contradict so-called intensity

---

[17] Since confirmed in experiments by H. Kohn [38].

rule III of the Utrecht school, according to which the intensity ratio between the two lines should have a value of 2.0.

REFERENCES

1. Ladenburg, R. and Reiche, F., Ann. Phys. 42, 181 (1913); see also Compt. Rend. 157, 279 (1913).

2. Ladenburg, R., Zeitschr. Phys. 4, 451, 469 (1921).

3. Roschdestwenski, D., Ann. Phys. 39, 307 (1915).

4. Senftleben, H., Ann. Phys. 47, 949 (1915).

5. Minkowski, R., Ann. Phys. 66, 206 (1921).

6. Füchtbauer, Chr. and Schell, K., Verh. Deutsch. Phys. Ges. 15, 974 (1913).

7. Gouy, G.L., Ann. Chim. Phys. 18(5), 5 (1879).

8. Bevan, P.V., Proc. Roy. Soc. 85, 66 (1911).

9. Roschdestwenski, D., Transact. Opt. Inst. Petrograd 2(13), 1-14 (1921).

10. Füchtbauer, Chr. and Hofmann, W., Ann. Phys. 43, 96 (1913).

11. Füchtbauer, Chr. and Bartels, H., Zeitschr. Phys. 4, 337 (1921).

12. Prokofjyev, A., Phil. Mag. 7, 1010 (1927).

13. Füchtbauer, Chr. and Meier, Phys. Zeitschr. 27, 853 (1926).

14. Burger, H.C. and Dorgelo, H.B., Zeitschr. Phys. 23, 258 (1924).

15. Dorgelo, H.B., Dissertation, Utrecht, 1921.

16. Bartels, H., Zeitschr. Phys. 26, 756 (1925).

17. Back, Dissertation, Tübingen, 1921.

18. Frerichs, R., Zeitschr. Phys. 31, 305 (1925).

19. Oudt, F.W., Zeitschr. Phys. 33, 656 (1925).

20. Jakob, H., Naturwissenschaften 13, 906 (1925).

21. Kohn, H. and Jakob, H., Phys. Zeitschr. 27, 819 (1926).

22. Filippov, A., Zeitschr. Phys. 26, 477 (1926).

23. Sommerfeld, A. and Heisenberg, W., Zeitschr. Phys. 11, 131 (1921).

24. Heisenberg, W., Zeitschr. Phys. 31, 617 (1926).

25. Ladenburg, R. and Reiche, F., Sitzungsber. Schles. Ges. Vaterl. Kultur, meeting of Feb. 24, 1914; see also Compt. Rend. 158, 1788 (1914).

26. Freundlich, H., Kapillarchemie [Capillary Chemistry], second edition, p. 1069.

27. Kohn, H., Ann. Phys. 44, 749 (1914).

28. Merton, T.R., Phil. Trans. 216, 459 (1921).

29. Weber, A.E., Ann. Phys. 45, 801 (1914).

30. Göos, F., Zeitschr. Phys. 31, 232 (1925).

31. Merton, T.R. and Nicholson, J.W., Phil. Trans. (ser. A) 217, 237 (1921).

32. Merton, Proc. Roy. Soc. 113, 697 (1927).

33. Leimbach, G., Zeitschr. Wiss. Photogr. 7, 18 (1909).

34. Senftleben, H. and Benedikt, E., Ann. Phys. 60, 297 (1919).

35. Beckmann, E. and Lindner, H., Zeitschr. Physikal. Chem. 82, 650 (1913).

36. Filippov, A., Zeitschr. Phys. 42, 495 (1927).

37. Hagenow, C.F. and Hughes, A.Ll., Phys. Rev. 30(2), 284 (1927).

38. Kohn, H., Phys. Zeitschr. 29, 49 (1928).